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Processing of Silicon Nitride Ceramics from Concentrated Aqueous Suspensions by Robocasting

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The optimization of concentrated AlliedSignal GS-44 silicon nitride aqueous slurries for robocasting was investigated. The dispersion mechanisms of GS-44 Si_3N_4 aqueous suspensions with and without polyacrylate were analyzed. The zero point of charge (ZPC) was at about pH 6. Well-dispersed GS-44 suspensions were obtained in the pH range from 7 to 11 by the addition of Darvan 821A. The influence of pH, amount of Darvan 821A and solids loading on the rheological behavior of GS-44 aqueous suspensions was determined. A coagulant, aluminum nitrate, was used to control the yield stress and shear thinning behavior of highly loaded Si_3N_4 slurries. Homogeneous and stable suspensions of 52 vol% GS-44 Si_3N_4 were robocast successfully at pH 7.8 to pH 8.5. The sintering process, mechanical properties and microstructural characteristics of robocast GS-44 bars were determined.

I. Introduction

Silicon nitride is considered to be a suitable ceramic for structural and advanced heat engine applications due to its excellent thermomechanical properties. However, the production cost of silicon nitride parts compared to similar metal parts or other advanced ceramics has remained prohibitive. Not only has the high purity ceramic powder used been expensive, but the shaping process to produce the desired parts has also been costly.[1-2] For this reason, in order to make complex-shaped silicon nitride components, injection molding,[3] slip[4] and pressure casting,[5] gel casting,[6] and direct coagulation casting[7] have been developed. While successful, these methods also have problems associated with production of molds, interactions with the mold material, cracking during their green-forming stages (i.e. casting, demolding and drying), binder removal, and long times from fabrication to final product.

Recently, robocasting [8,9] was developed at Sandia National Laboratories as an alternative shaping process. Robocasting is a new technique for freeform fabrication of dense ceramics from slurry deposition. Ceramic components with simple or complex shapes are rapidly produced from a CAD drawing directly to a finished component, and little or no machining is necessary after fabrication. In addition, robocasting is moldless and binderless, and fabrication rates are on the order of 1 cm^3 per minute. This process has been demonstrated to be effective with alumina and a variety of oxide ceramics.

The aim of this work was to develop aqueous silicon nitride suspensions that are suitable for robocasting. Robocasting requires the use of slurries with very high solids loading and carefully controlled rheology. Therefore, several fundamental aspects about the dispersion mechanisms and effects of dispersant, pH, additives and solids loading on

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the rheological behavior of Si_3N_4 aqueous suspensions were studied. Robocasting of aqueous Si_3N_4 slurries was optimized. Finally, the sintering process and microstructure of robocast bars were characterized.

II. Experimental Procedure

(1) Materials and Chemicals

The powder used in this study was high-purity α-Si_3N_4 powders (GS-44, Allied Signal Inc. Torrance, CA). The average particle diameter measured by an x-ray absorption/sedimentation technique was 0.77 μm. The average surface area as measured by standard BET N_2 adsorption was 7.7 m^2/g.

Darvan 821A (with 40% by weight of ammonium polyacrylate of molecular weight about 3500) obtained from R.T. Vanderbilt Company was used as a dispersant. The pH was adjusted with analytical grade nitric acid (1N) and ammonium hydroxide solutions (40%). Deionized water was used throughout this study.

(2) Sedimentation Tests

Sedimentation tests were conducted using 5 vol% Si_3N_4 aqueous suspensions. Various amounts of Darvan 821A were added to the suspensions which were then ball-milled for at least 12h. The pH values of the suspensions were adjusted and then the suspensions were poured into graduated cylinders, and after 5 days, the final sedimentation cake heights were recorded.

(3) Viscosity Measurements

Viscosity measurements were made with a rotary viscometer with a small sample chamber (Brookfield Model LVT, Stoughton, MA) or a concentric cylinder viscometer (Brookfield Model DV-III Rheometer, Stoughton, MA). The apparent viscosity was calculated as the ratio between the shear stress and the shear rate.

(4) Processing of Robocasting and Sintering

The robocast samples were prepared from 52 vol% suspensions containing additives at Sandia National Laboratories. The robocast bars were dried overnight at room temperature and were embedded in a powder bed, consisting of 50 wt% Si_3N_4 and 50 wt% BN, then sintered in a N_2 atmosphere at 1600~1800 °C by pressureless or pressure sintering. The samples were held at the maximum temperature for 1~2h. The sintered densities were measured by a standard water immersion method (ASTM C20). Fracture or etched surfaces of sintered robocast samples were observed using a scanning electron microscopy (SEM).

III. Results and Discussion

(1) Mechanism of Dispersion of Si_3N_4 with and without Polyelectrolyte

The zeta potential versus pH curve of the Si_3N_4 powder was determined by Liu[10]. The isoelectric point (IEP) is at about pH 6. At pH values higher than the IEP, the zeta potential becomes increasingly negative as pH increases from 6 to 10.5.[10] Typically colloids will form the most loosely packed flocculated structures near the IEP and more densely packed structures as the pH is changed away from the IEP. The stability (the degree of dispersion) of a suspension is controlled by the magnitude of the surface charge on the colloidal particles.

Fig. 1 shows the results of sedimentation tests for GS-44 silicon nitride suspensions as a function of both pH and percent dispersant, of Darvan 821A. Without any dispersant, the most flocculated sedimentation occurs between pH 5 and 6, in agreement with the IEP. As the pH is increased the sedimentation volume decreases to 4.5 ml. At pH values ≥ 9.6 there is no more appreciable decrease in the sedimentation volume. A sedimentation volume of 4.5 ml was arbitrarily chosen as a stability boundary. Suspensions prepared in the stable region are dispersed and result in dense settled structures while unstable suspensions result in flocculated structures. In the absence of dispersants, the GS-44 powder could be dispersed only at pH values ≥ 9.6 when the particles are appreciably negatively charged and induce electrostatic repulsion. However, for practical reasons silicon nitride should not be processed in alkaline conditions because hydrolysis reactions promote the formation and dissolution of silica.[11]

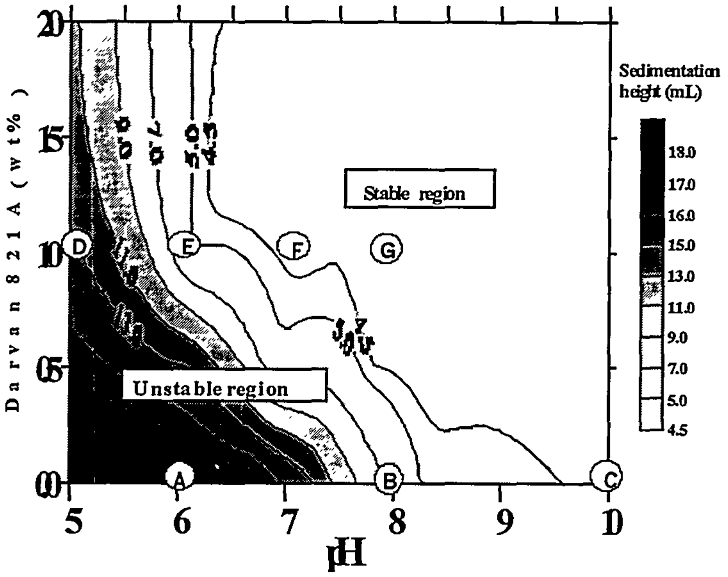


Fig. 1. The relationship between pH, Darvan 821A and sedimentation height (5 vol% GS-44 Si_3N_4), points at A, B, C, D, E, F, and G are used to clarify rheological behavior and the data represented in Figure 2.

The effect of the dispersant Darvan 821A on the sedimentation behavior of the Si_3N_4 powder is also represented in Fig. 1. Figure 1 shows that the addition of 1 wt% Darvan 821A can significantly enlarge the pH range for forming stable suspensions down to pH 6.5. Further additions of polyacrylate up to 2 wt% do not significantly improve dispersion and do not further enlarge the pH range for stability. In summary, 1 wt% Darvan 821A is efficient for the dispersion of this Si_3N_4 powder in an aqueous medium under benign pH conditions. This is understood to be the result of ammonium polyacrylate adsorption onto the Si_3N_4 particles. The adsorbed polyelectrolyte can induce stabilization as long as it is appreciably dissociated (ionized) and therefore negatively charged.[12] Below pH 6 even the addition of excess dispersant has no measurable contribution to dispersion because the adsorbed dispersant on powder surfaces is not appreciably ionized.

The Darvan 821A (ammonium polyacrylate) dissociates into a negatively charged polymer according to the reaction:

$$RCOONH_4 \Leftrightarrow RCOO^- + NH_4^+$$

The fraction of $RCOONH_4$ groups that dissociate into negative $RCOO^-$ groups is dependent on the pH. The fraction dissociated (α) is nearly zero at pH 3.5 and increases to $\alpha = 1$ near pH 8.[13]

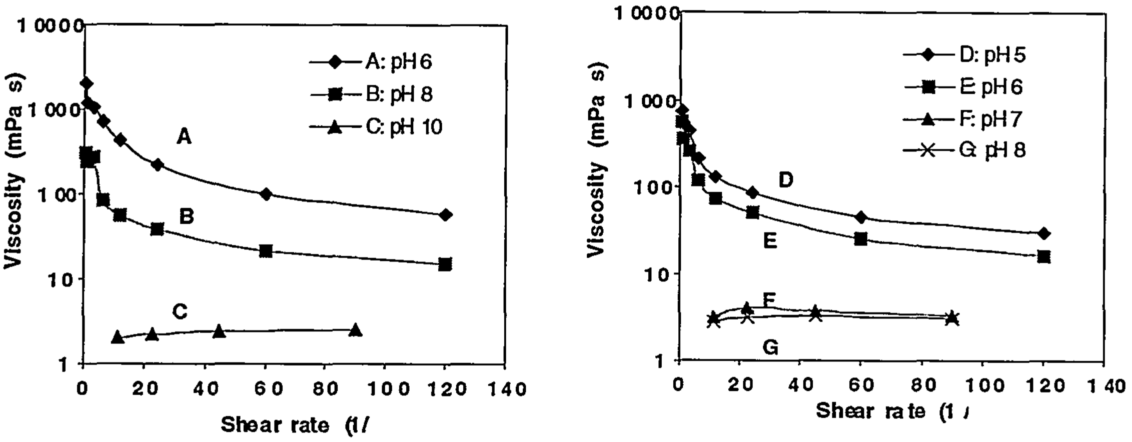
The adsorption of ammonium polyacrylate on Si_3N_4 is dependent on the fraction dissociated, the number of positive adsorption sites on the Si_3N_4, and the equilibrium concentration of free non-adsorbed polyacrylate in solution. The most efficient dispersion of Si_3N_4 with ammonium polyacrylate is defined as being the pH at which stable suspensions exist while the amount of free non-adsorbed polyacrylate is kept to a minimum. This condition can be intuitively estimated to occur at pH 7 – 8. At pH values ≤ 6.5 the adsorbed polyacrylate does not have enough dissociated functional groups to induce reliable stabilization (see Fig. 1). At pH values ≥ 8.5 stable suspensions exist however the polyacrylate is only weakly adsorbed onto the Si_3N_4 and a large fraction of the polyacrylate remains non-adsorbed in solution. Efficient adsorption and good stabilization occurs in the pH range of 7-8. Si_3N_4 still has an appreciable number of adsorption sites while the polyacrylate is also nearly fully negatively charged. It is in this range that enhanced interfacial charge and stabilization results due to adsorption of the charged polyacrylate. Therefore, in addition to electrostatic interactions, steric interactions arise from overlap of the adsorbed layers. The results of these interactions can be repulsive or attractive in nature depending on whether or not the outermost layers on the particles prefer to be in contact with the aqueous medium.[14] Therefore, the positive contribution of the steric interaction of the adsorbed polyacrylate is attributed to the hydrophilic nature of the polyacrylate. Further, the dispersion functions of the adsorbed polyacrylate are believed to arise from the two oxygen atoms in the carboxylic group, $-COO^-$, of the polyacrylate. The charged oxygen atom in the carboxylic group is responsible for the measured interfacial charge properties of the modified powder, while the uncharged oxygen atom has an additional contribution to the hydrophilic nature of the adsorbed layer[10].

(2) Rheology of Robocasting Slurries

Fig. 2 shows the effects of pH and Darvan 821A on viscosity and rheological behavior for 20 vol% GS-44 Si_3N_4 suspensions. In Fig. 2 (a), a slurry formulated at pH 10 with no added dispersant (curve C) has a low viscosity and is nearly Newtonian, because there is a strong, electric double-layer repulsion between the silicon nitride particles, which inhibits agglomeration. A slurry formulated at pH 6 (the IEP) with no dispersant (curve A) exhibits a much higher viscosity at all shear rates, and its viscosity decreases (shear thins) with increasing shear rate. No repulsive force exists at pH 6, and large attractive van der Waals forces produce an attractive, touching particle network. At pH 8 (curve B), the slurry exhibits shear-thinning behavior and intermediate viscosities. Firth and Hunter[15] describe a number of mechanisms to explain the viscosity of particulate slurries. When the network is sheared, it breaks into agglomerates that decrease in size with increasing shear rate. The liquid within each agglomerate is relatively immobile since it must flow with the agglomerate. Based on this model, it can be explained that the decrease in viscosity with increasing shear rate is result of the increasing liquid volume released by the agglomerates as they become smaller.

As shown in Fig. 2 (b), the addition of 1 wt% Darvan 821A to the slurry formulated at pH 5 (curve D) or pH 6 (curve E) reduces the viscosity of slurry at all shear rates, but the rheology remains shear-thinning. If the pH is increased further, such as pH 7 (curve F) or pH 8 (curve G), the viscosity decreases by an order of magnitude and the rheology becomes nearly Newtonian. Because the adsorbed dispersant decreases the attractive forces between the silicon nitride surfaces, the presence of dispersant should allow the network to be broken into smaller agglomerates at a given shear rate relative to the strong network formulated without the added dispersant. The viscosity decreases with an increases in pH and low viscosity occurs at pH > 7. The low viscosities are attributed primarily to enhanced electrostatic repulsion between the dispersant-adsorbed particles. The steric interaction of the adsorbed polyacrylate has a positive contribution to dispersion as well. This is attributed to the hydrophilic nature of the polyacrylate. For pH < 7, high viscosity is related to a decrease in the negative charge characteristics of the adsorbed polyelectrolyte and a decrease in the electrosteric repulsive barrier between particles[10]. Hence, the GS-44 Si_3N_4 powder with Darvan 821A at pH 7~11 is well dispersed and has a low viscosity. This result is in agreement with Liu[10] and Albano[16].

As shown in Fig. 1 and Fig. 2, slurries with low viscosity and Newtonian rheology (C, F, and G in Fig. 2) are located at the stable region in Fig. 1, but slurries with higher viscosity and shear-thinning rheology (A, B, D, and E in Fig. 2) are located in the unstable region in Fig. 1. Although a well-dispersed slurry without Darvan at pH 10 can be made, the dissociation of surface groups of Si_3N_4 may be appreciable at this pH. Thus, addition of 1 wt% Darvan 821A at pH 7 ~ 8 is preferred for well-dispersed Si_3N_4 slurries to be used for part fabrication.



(a) no Darvan 821A (b) 1 wt% Darvan 821A

Fig. 2. Effects of pH and Darvan 821A on viscosity and rheological behavior for 20 vol% GS-44 Si_3N_4 suspensions.

In production it is desirable to use slurries with a high solids loading however the magnitude of viscosity increases as the solids loading increases. It has been found that when the solids content of silicon nitride slurries exceed about 47 vol%, the slurry becomes extremely dilatant and ceases to flow[17]. Hence, conventional silicon nitride slurries for slip-casting typically utilize a solids content of less 47 vol%. Here, Fig. 3 shows that suspensions as high as 55 vol% Si_3N_4 may be formulated. Figure 3 also shows that as the volume percent solids increases, a pH ≥8 must be maintained to still have workable suspensions. Fig. 4 illustrates the rheological behavior of dispersed GS-44 Si_3N_4 slurries with various solids contents at pH 8.5 and Fig. 5 shows the effect of solids loading on viscosity. At low solids loading, dispersed slurries exhibit very low viscosity and are rheologically Newtonian. Around 30 vol% solids, the slurries begin to show shear-thinning (pseudoplastic) behavior, even though the viscosity is still relatively low. As the solids content approaches 50 vol%, interparticle interactions and inter-particle collisions become dominant; viscosity begins to increase appreciably, and the rheological behavior becomes highly shear-thinning. At approximately 55 vol% percent solids, particle mobility becomes restricted, and the slurry locks up into a shear-thickening (dilatant) mass.

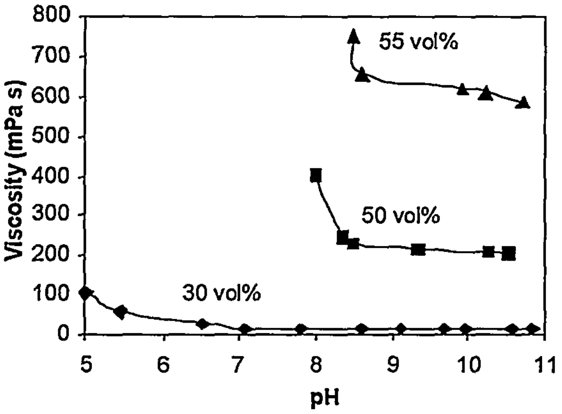


Fig. 3. Viscosity at shear rate 24 s^{-1} versus pH for GS-44 Si_3N_4 suspensions from 30 to 50 vol% solids concentrations. (1 wt%Darvan 821A)

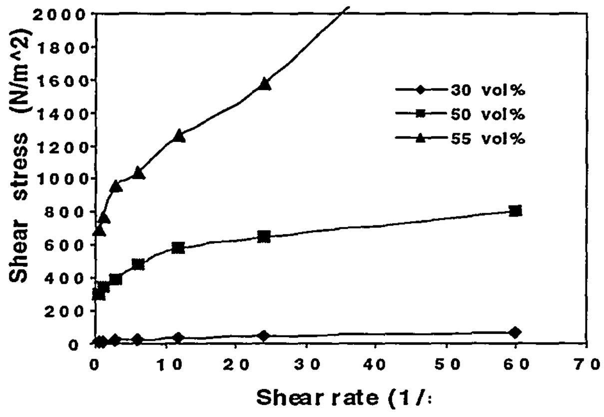


Fig. 4 Shear stress versus shear rate for different solids loading slurries with 1 wt% Darvan 821A at pH 8.5.

For optimal robocasting, it is desirable to robocast with slurries that have solids loadings close to the dilatant transition.[8,9] A high solids content minimizes the amount of drying shrinkage and sintering shrinkage so that final bead dimensions and final near-net-shape tolerance can be more accurately controlled. How close a slurry is to its pseudoplastic/dilatant transition will affect the proper choice of extrusion rate. In addition to solids content a robocasting slurry must also have a rheology that is shear-thinning but with an appreciable yield stress.

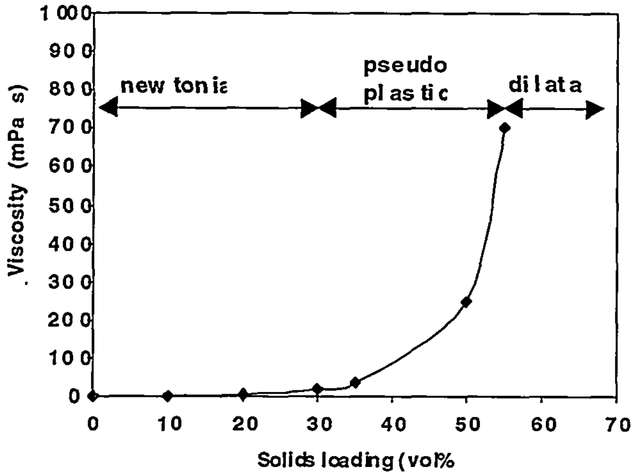


Fig. 5. Viscosity versus solids loading behavior for dispersed GS-44 slurries at 1 wt% Darvan 821A and pH 8.5 shear rate 24 s^{-1}).

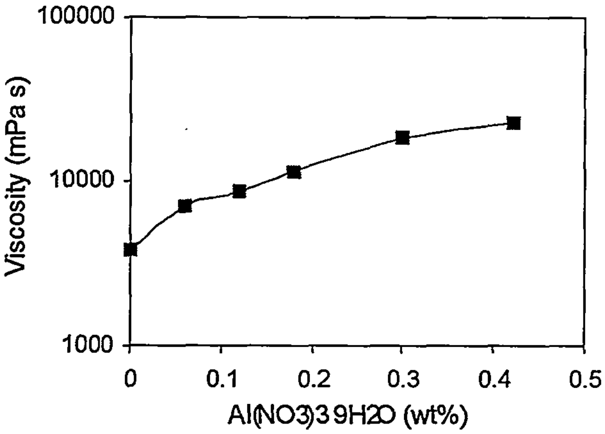


Fig. 6. Viscosity as a function of amount of Al-nitrate at 52 vol% GS-44, 1 wt% Darvan 821A, pH 8 and shear rate 2.5 s^{-1}.

In order to control the yield stress of concentrated GS-44 Si_3N_4 slurries for robocasting, additions of aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$] can be used. Silicon nitride slurries made of 52 vol% GS-44 powder and 1wt% Darvan 821A with varying amounts of aluminum nitrate based on the mass of GS-44 powder were evaluated. The pH was controlled at constant value, pH=8. The viscosity of slurries increases with increasing amounts of aluminum nitrate (Fig. 6). The viscosity is too high to measure when the addition of aluminum nitrate exceeded 0.4 wt%. Aluminum nitrate acts as a coagulant. The aluminum nitrate modifies the interparticle forces, agglomerate structure, and consistency of the slurry. Too much aluminum nitrate fully coagulated the slurries which accounts for the increase in overall viscosity. Fig. 7 shows the rheology changes between the pure and 0.4 wt% aluminum nitrate GS-44 slurries. The 52 vol% slurry with 0.4 wt% aluminum nitrate at pH 8 is an example of a slurry with a Bingham plastic rheology and suitable for robocasting.

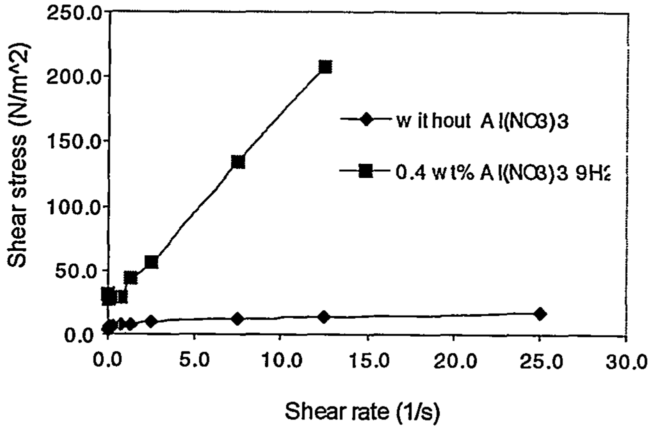
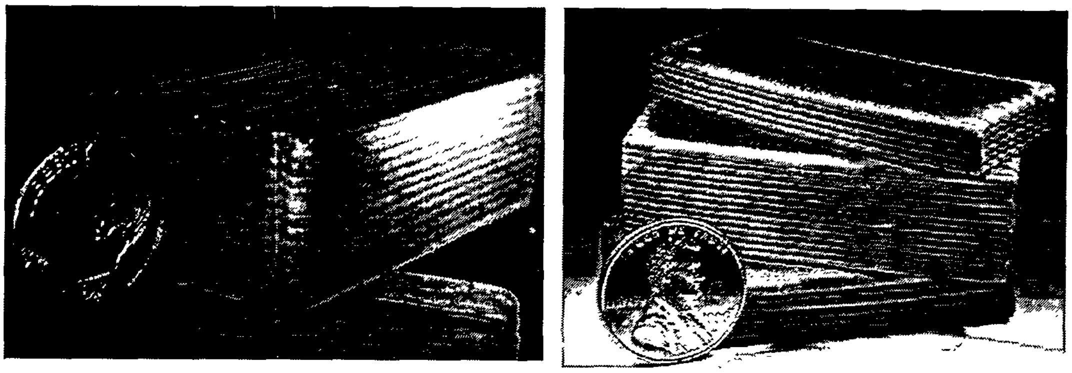


Fig. 7. Relationships between shear stress and shear rate with and without Al-nitrate at 52 vol%GS-44, 1 wt% Darvan821A at pH 8.



(a) (b)

Fig. 8. Robocast GS-44 Si_3N_4 bars, (a) green; (b) sintered.

(3) Robocasting and Sintering of GS-44 Si_3N_4

GS-44 Si_3N_4 bars, up to 20x30x65 mm in size, have been robocast successfully. The rheological studies previously discussed were used to determine the optimal conditions for robocasting. They were 52 vol% GS-44 Si_3N_4, 1 wt% Darvan 821A, 0.4wt% aluminum nitrate and pH 7.8~8. No cracking and minimal warping were observed during robocasting, drying, and sintering (Fig. 8). The green density was 1.80 g/cm^3 (or 56% of theoretical).

Densification of GS-44 by pressureless sintering was maximum at 1700 °C as shown in Fig. 9 and resulted in linear shrinkage of approximately 17%. The relative density obtained at 1700 °C after 1h was 98.5% of theoretical. This result is very encouraging because pressureless sintered Si_3N_4 usually exhibits limited densities due to residual porosity.[18] A sintered density, higher than 99.6% of theoretical, was obtained for the same samples by pressure sintering in a 3.4E5 Pa (50 psi) N_2 atmosphere at 1800 °C for 1h. There is no apparent cracking and the overall color is fairly uniform. Fig. 8 b shows the sintered robocast bars.

(4) Mechanical Properties and Microstructure

The average flexural strength and hardness of pressure sintered robocast GS-44 samples are shown in Table I and are comparable to the standard properties of slip cast GS-44. Sintered GS-44 samples primarily contain the β-Si_3N_4 phase as shown by x-ray diffraction in Fig. 10. Polished and etched GS-44 has large elongated β-Si_3N_4 grains as shown in Fig. 11. After flexural strength measurements were completed the fracture surfaces were examined using SEM. Fig. 12 a shows significant pullout of β-Si_3N_4 fibers from the fracture surfaces. Regular hexagonal cross-sections of β-Si_3N_4 crystals are clearly shown in Fig. 12 b. They are microstructural characteristics of typical dense Si_3N_4 ceramics and are believed to be responsible for the superior mechanical properties of Si_3N_4 ceramics.

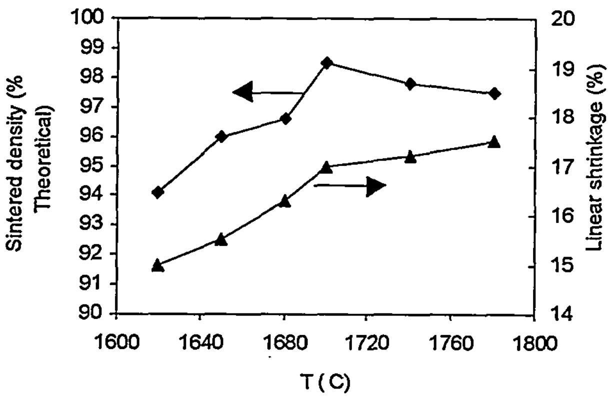


Fig. 9. Densification of robocast GS-44 ceramics by pressureless sintering.

Table I. Comparison of mechanical properties between robocasting and conventional product

Property	Robocast GS-44	AlliedSignal Slipcast GS-44 SL[8]
Density (g/cm^3)	3.22	3.2
Flexural Strength (MPa, @ RT)	735±38	759
Hardness (Vickers, GPa)	14.74±0.51	14.31

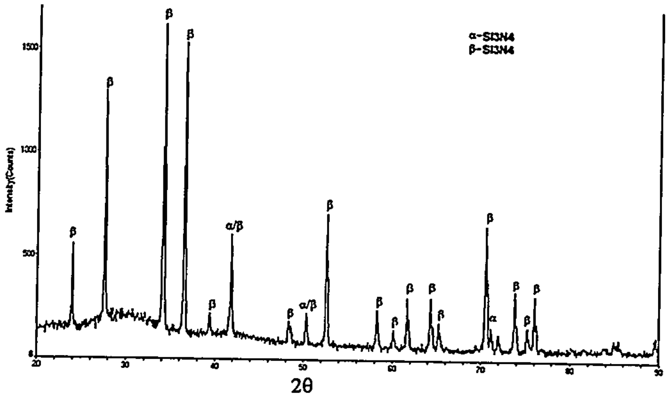


Fig. 10. X-ray diffraction pattern of sintered robocast GS-44

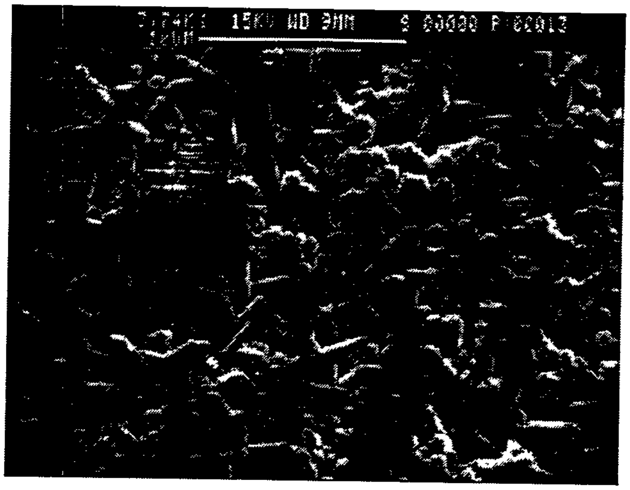
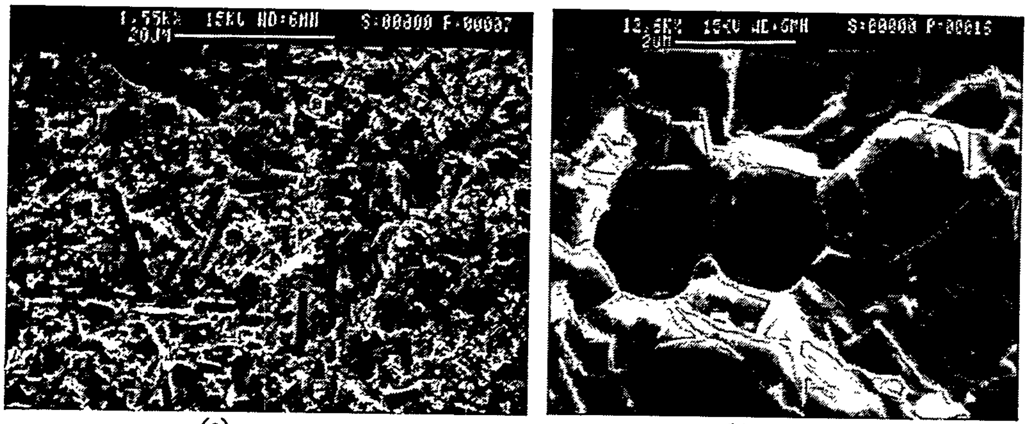


Fig. 11. Microstructure of sintered robocast GS-44.



(a)

(b)

Fig. 12. Pullout β-Si_3N_4 fibers in the fracture surfaces of sintered GS-44 bars (a) and cross-section of β-Si_3N_4 fibers (b).

IV. Conclusions

(1). The GS-44 silicon nitride powder exhibits a zero point of charge (ZPC) at pH 6. It can be dispersed only at a pH ≥ 9.6 without dispersants.

(2). Well-dispersed GS-44 suspensions can be obtained at pH 7~11 range by the addition of Darvan 821A. This is attributed primarily to the enhanced electrosteric repulsion between the dispersant-adsorbed particles. In addition to the electrostatic interaction, the steric interaction of the adsorbed polyacrylate has a positive contribution to dispersion. This is attributed to the hydrophilic nature of the polyacrylate.

(3). The viscosity of GS-44 slurry decreases with an increase in pH. At low pH, near the ZPC, the slurry exhibits a very high viscosity because no repulsive force exists between the particles. The viscosity also decreases with Darvan 821A additions, but an adequate amount of polyacrylate, 1 wt% Darvan 821A, was determined.

(4). The viscosity of GS-44 slurry increases with increasing solids loading. The rheological behavior of a dispersed GS-44 slurry in an alkaline pH range is Newtonian at solids loading less than 30 vol%, pesudoplastic in the range from 30 vol% to 55 vol%, and approaches dilatancy above 55 vol%. Working with slurries that are close to the pseudoplastic/dilatant transition is desirable for robocasting. It is also important to use slurries that have an appreciable yield stress. Aluminum nitrate can be used as a coagulant for GS-44 Si_3N_4 slurries and induce a yield stress and a Bingham plastic flow behavior at high solids loading.

(5). GS-44 Si_3N_4 aqueous slurry has been successfully robocast. The green density, 56% of theoretical, was achieved from robocasting of 52 vol% GS-44 aqueous slurry. The GS-44 robocast bars can be densified by pressureless or pressure sintering. Sintered density of 98.5% of theoretical was obtained by pressureless sintering and 99.6% of theoretical with pressure sintering.

(6). Mechanical properties of robocast GS-44 were compared favorably with products produced conventionally. Flexural strength of 737 MPa and Vickers hardness of 14.74 GPa were obtained at room temperature. The microstructure of sintered robocast bars shows interlocking elongated β-Si_3N_4 grains.

Acknowledgement

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